

Chapter 38 - SANS FROM POLYMER BLENDS

Polymer blends are mixtures of homopolymers for which mixing happens at the molecular level. Two polymers mix only when they are compatible with each other (i.e., when their chemical units are similar) and when they correspond to conditions in the mixed region of the phase diagram. The process of polymer blends demixing (phase separation) is discussed.

1. THE FLORY-HUGGINS MODEL

Polymer thermodynamics are described by the Gibbs free energy density which consists of two main contributions: an entropic part (combinatorial mixing of the monomers) and an enthalpic part (interactions between monomers). The Flory-Huggins equation for polymer blends gives a simple expression for the Gibbs free energy density:

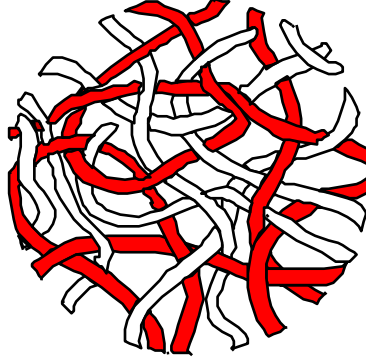
$$\frac{G}{k_B T} = \frac{\phi_1}{n_1 v_1} \ln(\phi_1) + \frac{\phi_2}{n_2 v_2} \ln(\phi_2) + \frac{\chi_{12}(T)}{v_0} \phi_1 \phi_2. \quad (1)$$

n_1 , ϕ_1 and v_1 are the degree of polymerization (i.e., number of monomers per chain), volume fraction and specific volume for monomer 1 and n_2 , ϕ_2 and v_2 are the equivalent quantities for monomer 2. χ_{12} is the usual Flory-Huggins interaction parameter and v_0 is a “reference” volume. Note that $\phi_1 + \phi_2 = 1$.

The SANS technique is sensitive to composition fluctuations and is therefore a good monitor of phase separation thermodynamics. The scattering intensity is related to the second derivative of the Gibbs free energy density with respect to composition. The scattering function in the forward direction ($Q = 0$) is given by:

$$S^{-1}(Q=0) = \frac{1}{k_B T} \frac{\partial^2 G}{\partial \phi_1^2} = \frac{1}{n_1 \phi_1 v_1} + \frac{1}{n_2 \phi_2 v_2} - 2 \frac{\chi_{12}(T)}{v_0}. \quad (2)$$

Phase separation thermodynamics are buried in the temperature-dependent Flory-Huggins parameter χ_{12} .



Polymers Blend

Figure 1: Schematic representation of a polymer blend mixture.

2. BINODAL AND SPINODAL LINES

The phase separation thermodynamics of polymer mixtures is characterized by two lines: the **binodal** and the **spinodal** lines. The **binodal line** corresponds to **generalized phase separation** (at large length scales) and the **spinodal line** corresponds to the onset of **density fluctuations** (at local length scales) leading the phase separation. The region between the binodal and spinodal lines is referred to as the **nucleation-and-growth region**.

The **chemical potential μ_1** is the first derivative of the Gibbs free energy density G with respect to the volume fraction ϕ_1 :

$$\frac{\mu_1}{k_B T} = \frac{1}{k_B T} \frac{\partial G}{\partial \phi_1} \quad (3)$$

$$\frac{\mu_1}{k_B T} = \frac{1}{n_1 v_1} \log(\phi_1) + \frac{1}{n_1 v_1} - \frac{1}{n_2 v_2} \log(1 - \phi_1) - \frac{1}{n_2 v_2} + \frac{\chi_{12}(T)}{v_0} (1 - \phi_1) - \frac{\chi_{12}(T)}{v_0} \phi_1$$

The **binodal** phase separation **line** is obtained when **the two minima of $G(\phi_1)$ have the same tangent slope line**.

The **osmotic pressure π_1** corresponds to the second derivative of G with respect to ϕ_1 :

$$\frac{\pi_1}{k_B T} = \frac{1}{k_B T} \frac{\partial^2 G}{\partial \phi_1^2} = \frac{1}{n_1 \phi_1 v_1} + \frac{1}{n_2 (1 - \phi_1) v_2} - 2 \frac{\chi_{12}(T)}{v_0}. \quad (4)$$

This expression also represents the inverse of the structure factor in the forward direction $S^{-1}(Q=0)$. The spinodal phase transition line is obtained when the condition $\pi_1=0$ (or $S(Q=0) \rightarrow \infty$) is met, i.e., it corresponds to the inflection points on the $G(\phi_1)$ curve.

3. THE RANDOM PHASE APPROXIMATION

The Random Phase Approximation (RPA) model is a mean field theory that describes polymer mixtures in the homogeneous phase region. It is a generalization of the Flory-Huggins equation to finite momentum transfer Q .

$$S^{-1}(Q) = \frac{1}{n_1 \phi_1 v_1 P_1(Q)} + \frac{1}{n_2 (1-\phi_1) v_2 P_2(Q)} - 2 \frac{\chi_{12}(T)}{v_0} \quad (5)$$

$P_1(Q)$ is the so-called Debye function for Gaussian random polymer coils.

$$P_1(Q) = \frac{2}{Q^4 R_{g1}^4} \left[\exp(-Q^2 R_{g1}^2) - 1 + Q^2 R_{g1}^2 \right]. \quad (6)$$

R_{g1} is the radius of gyration for component 1. The radius of gyration can be expressed in terms of the statistical segment length a_1 (think monomer size) as $R_{g1}^2 = na_1^2/6$. Precisely, the statistical segment length is the length for which the polymer chain is represented by a random walk. The Debye function is used because chains in compatible polymer blends do not swell or collapse.

The SANS scattering cross section is given in terms of an absolute macroscopic cross section (units of cm^{-1}) as:

$$\frac{d\Sigma(Q)}{d\Omega} = \left(\frac{b_1}{v_1} - \frac{b_2}{v_2} \right)^2 S(Q) \quad (7)$$

where b_1/v_1 is the scattering length density for monomer 1 and the term $(b_1/v_1 - b_2/v_2)^2$ is the contrast factor. This scattering cross section is also referred to as the scattering intensity $I(Q)$.

4. POLYOLEFIN BLENDS

Polyolefins are a wide class of polymeric materials that find uses in many aspects of our daily lives. These are polymers containing C=C double bonds either in an aromatic ring or in the aliphatic chain. These double bonds can be saturated (i.e., broken) through the hydrogenation process. Gentle interactions among polyolefin blend mixtures make them ideal “mean field” systems to investigate phase separation thermodynamics. The mixed one-phase region is easily accessible for a wide range of temperatures and compositions.

Polyolefin blends are characterized by an Upper Critical Spinodal Temperature (UCST); i.e., they phase separate upon cooling. Phase separation occurs either by spinodal decomposition (sinusoidal composition fluctuations) or by nucleation and growth (phase coarsening around nucleating centers). The SANS method is used here to map out the spinodal temperature for a polyolefin blend mixture.

5. A POLYOLEFIN BLEND

The polyolefin blend system considered here is polyethylbutylene mixed with deuterated polymethylbutylene (hPEB/dPMB) (Lefebvre et al, 2000). The PMB polymer is deuterated for enhanced neutron contrast. The chemical formula for hPEB is $[-CH_2-CH(C_2H_5)-CH_2-CH_2-]$ and for dPMB is $[-CHD-CD(CH_3)-CD_2-CHD-]$. An hPEB/dPMB polymer blend with molecular weights of $M_w = 40,100$ g/mol and 88,400 g/mol and composition of $\phi_{hPEB} = 0.57$ and $\phi_{dPMB} = 0.43$ was measured by SANS. The stoichiometry of this sample is C_6H_{12} for hPEB and close to $C_5H_{4.5}D_{5.5}$ for dPMB as measured by NMR.

The scattering intensity at various temperatures is shown below. Scattering increases for decreasing temperature, due to the approach to the phase transition (spinodal) line.

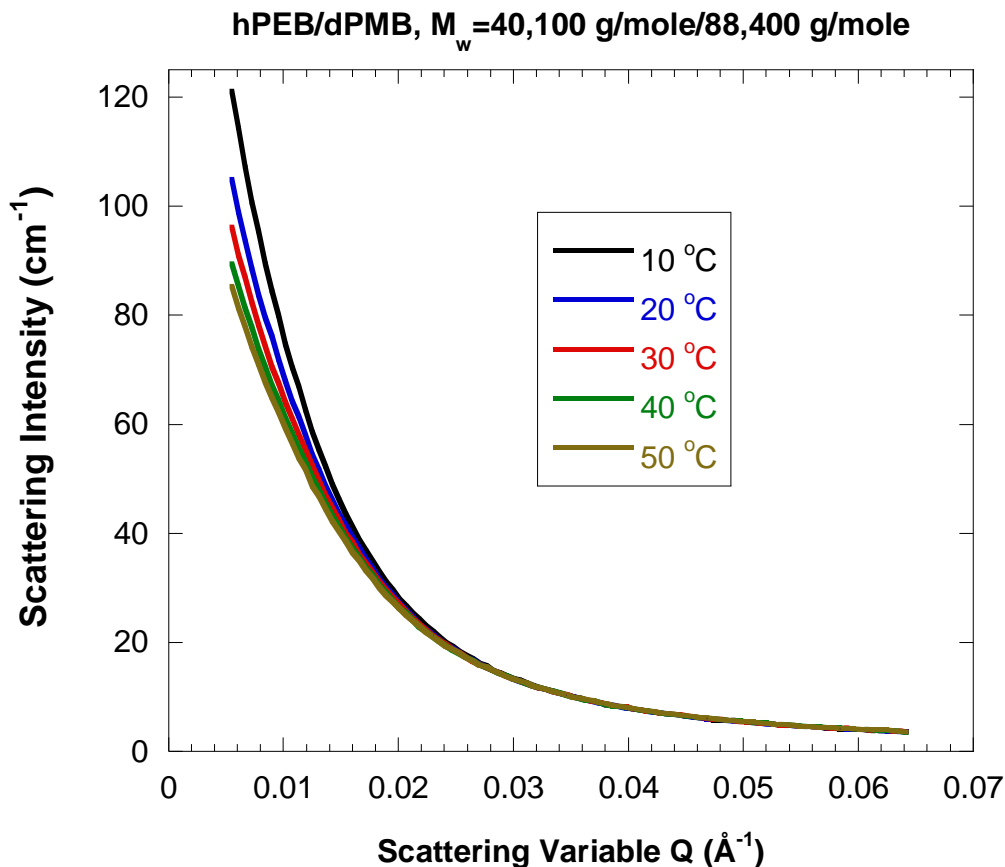


Figure 2: SANS **scattered intensity** for the hPEB/dPMB sample at various temperatures. The intensity increases as the temperature is lowered (UCST system)

The **Zimm plot** ($I^{-1}(Q)$ vs Q^2) yields an extrapolated value of the forward scattering $I(Q = 0)$.

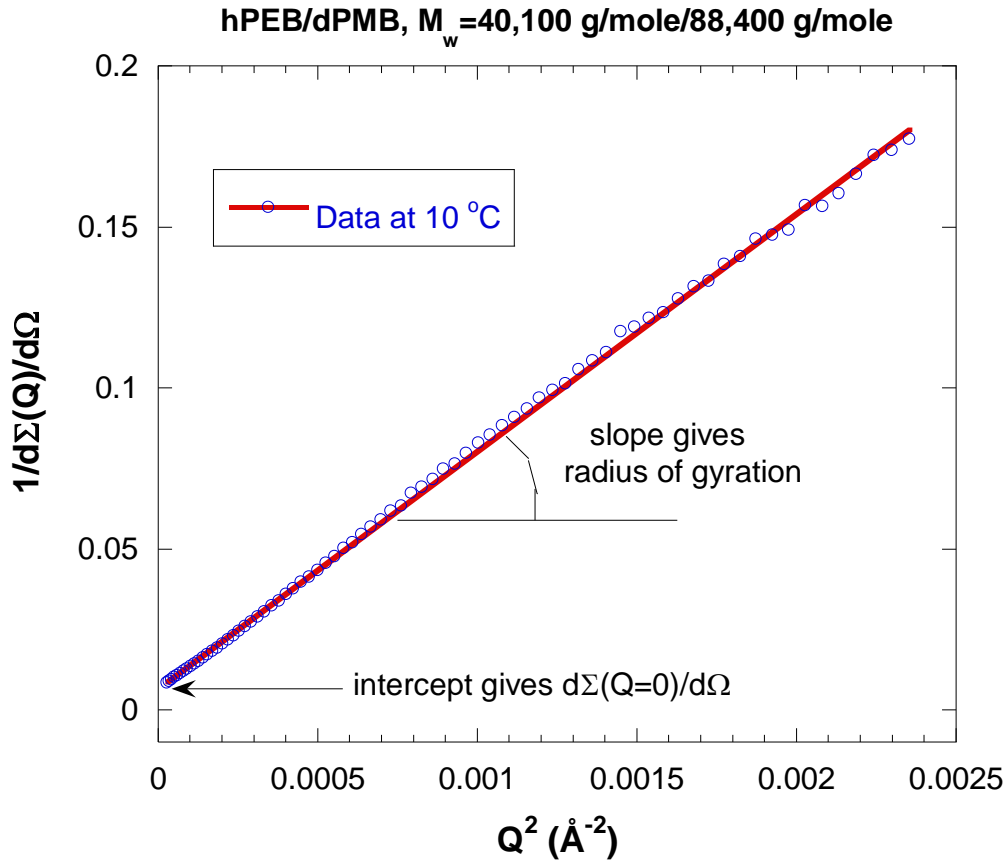


Figure 3: The **Zimm plot** yields $I(Q=0)$ for the intercept.

A **plot of $I^{-1}(Q=0)$ vs T^{-1}** (T is in K) **yields the spinodal temperature from the intercept;** i.e., when $I(Q=0)$ diverges or $I^{-1}(Q=0)$ is equal to zero. An estimated spinodal temperature of 220 K = -53 °C is obtained for this sample.

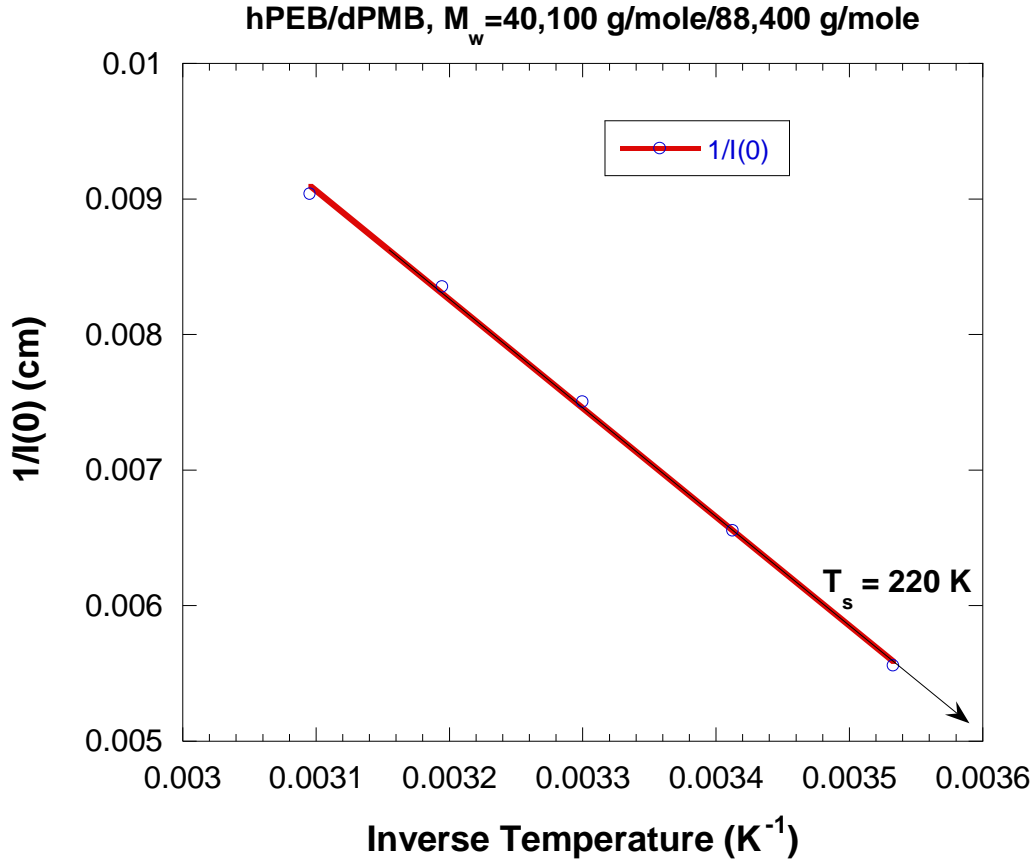


Figure 4: Variation of the inverse intensity (extrapolated to $Q = 0$) with the inverse temperature (in degree K). The **spinodal temperature** is obtained for $1/I(0)=0$.

The reduced SANS data for every temperature were **fit to the RPA functional form** for the binary blend mixture with the following input parameters:

Degrees of polymerization:	$n_1 = 525$	$n_2 = 1105$
Volume fractions:	$\phi_1 = 0.57$	$\phi_2 = 0.43$
Specific volumes:	$v_1 = 97.5 \text{ cm}^3/\text{mol}$	$v_2 = 81.9 \text{ cm}^3/\text{mol}$
Scattering lengths:	$b_1 = -4.99 \times 10^{-13} \text{ cm}$	$b_2 = 53.1 \times 10^{-13} \text{ cm}$

The specific volumes were obtained as the ratios of the monomer molecular weights to their densities. Note that the scattering length for hPEB is negative whereas that for dPMB is positive.

Fit results are:

Segment lengths:	$a_1 = 8 \text{ \AA}$	$a_2 = 8 \text{ \AA}$
Interaction parameter:	$\frac{\chi_{12}(T)}{v_0} = \frac{0.0106}{T} - 1.84 \times 10^{-5} \text{ (T in deg K).}$	

The approach used here is approximate. The specific volumes were assumed to be independent of temperature. The purpose of the argument being made here is to show how the Flory-Huggins theory could be used to obtain a phase diagram. Note that in this approach, the “reference” volume v_0 needs to be specified only if $\chi_{12}(T)$ needs to be known. In this case, v_0 is approximated as $v_0 = \sqrt{v_1 v_2}$.

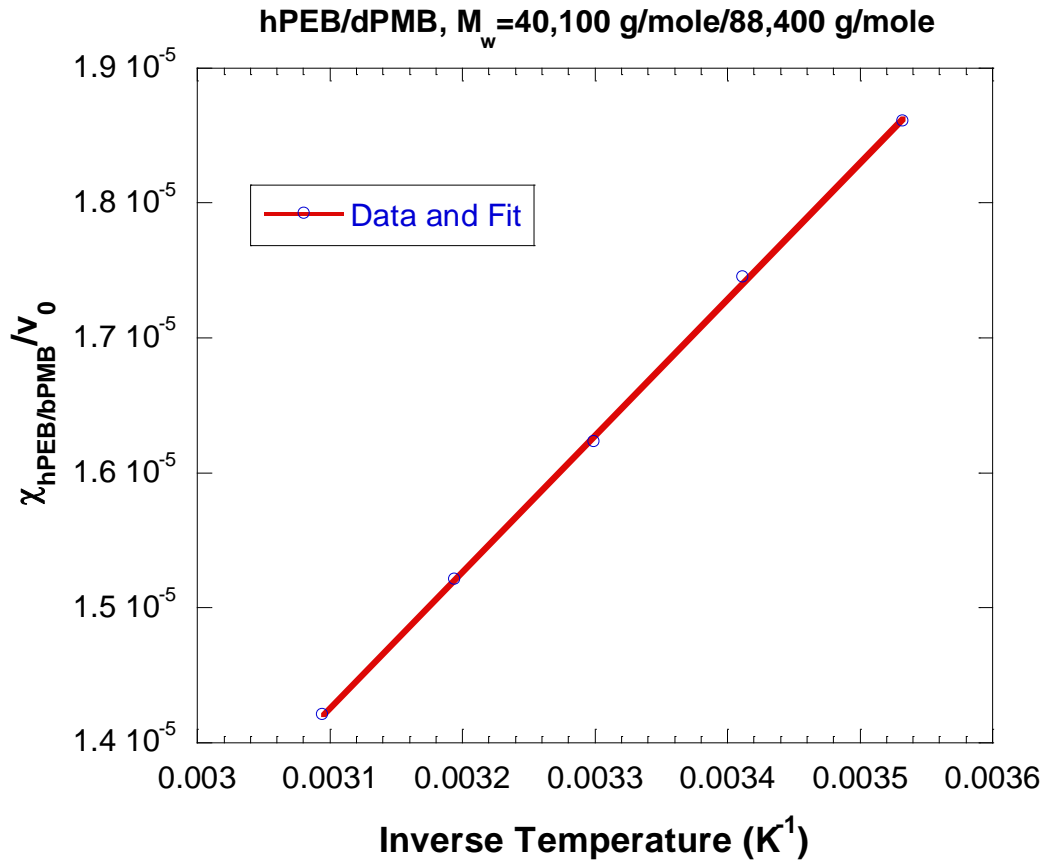


Figure 5: Variation of the Flory-Huggins $\frac{\chi_{12}(T)}{v_0}$ parameter with inverse temperature.

6. GIBBS FREE ENERGY DENSITY AND PHASE DIAGRAM

Based on the Flory-Huggins parameter obtained from one hPEB/dPMB sample, the Gibbs free energy density and the phase diagram can be constructed. This assumes that the Flory-Huggins parameter does not depend on polymer blend composition. This is a fairly good assumption for polyolefin blends.

Based on the figure showing the Gibbs free energy density, the 220 K (= -53 °C) temperature corresponding to the spinodal temperature of this sample is also the critical temperature of the phase diagram. The 270 K temperature is well in the one-phase region and the 200 K temperature is well into the spinodal region. The spinodal points are located at the two inflection points (where the second derivation of the free energy is

zero). The two **binodal points** correspond to two-points on the curve that share the same tangent as shown in the figure.

Recall that the **spinodal condition** is given by:

$$\frac{1}{k_B T} \frac{\partial^2 G}{\partial \phi_1^2} = \frac{1}{n_1 \phi_1 v_1} + \frac{1}{n_2 \phi_2 v_2} - 2 \frac{\chi_{12}(T)}{v_0} = 0. \quad (8)$$

The **binodal condition** is obtained for:

$$\frac{G(\phi_A) - G(\phi_B)}{\phi_A - \phi_B} = \frac{\partial G(\phi_A)}{\partial \phi_1} = \frac{\partial G(\phi_B)}{\partial \phi_1}. \quad (9)$$

At fixed T, the two binodal volume fractions are called ϕ_A and ϕ_B .

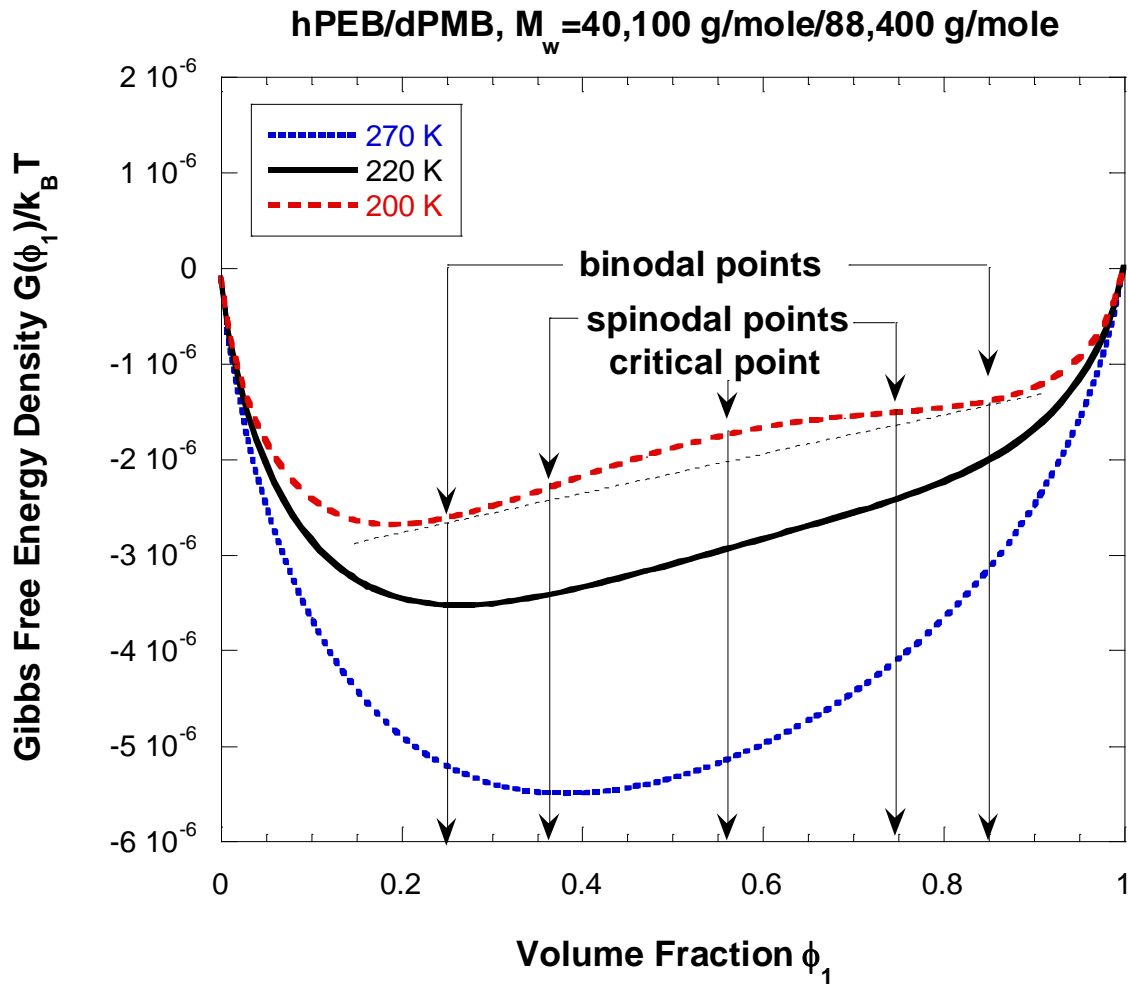


Figure 6: Variation of the Gibbs free energy density with volume fraction $\phi_1 = \phi_{\text{hPEB}}$ for hPEO/dPMB blends. The measured sample with 0.57/0.43 volume fraction is at the critical point.

Once the Gibbs free energy density is known, the demixing phase diagram can be mapped out.

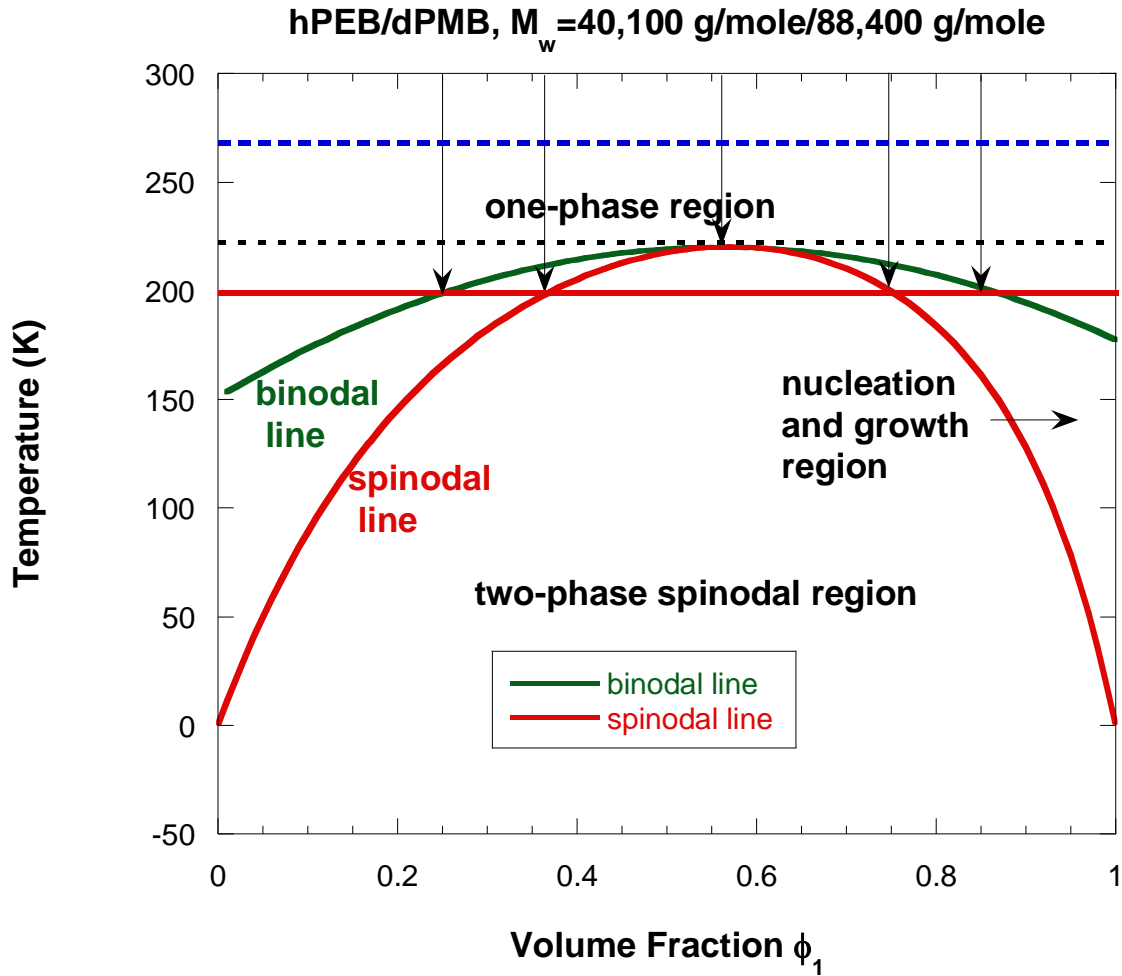


Figure 7: Variation of the spinodal and binodal temperatures with volume fraction $\phi_1 = \phi_{\text{hPEB}}$ for hPEO/dPMB blends. The spinodal region is underneath the binodal line. Vertical lines continue from the previous figure.

REFERENCES

A.A. Lefebvre, J.H. Lee, N.P. Balsara, B. Hammouda, "Fluctuations in Highly Metastable Polymer Blends", J. Polym. Sci., Polym. Phys. Ed. 38, 1926-1930 (2000).

QUESTIONS

1. What scattering method detects the spinodal temperature? How about the binodal temperature?
2. What equation relates scattering methods and polymer mixture thermodynamics?
3. What relation defines the spinodal condition?
4. Based on the Flory-Huggins theory of phase separation, can you guess what would be the main difference between phase diagrams for a polymer blend and a polymer solution?
5. Polymer phase separation occurs either through spinodal decomposition or nucleation and growth? Define these two regions of the phase diagram.
6. Does the RPA apply when the sample is in the two-phase region?
7. What is the morphology characteristic of a fully phase separated polymer blend?

ANSWERS

1. The spinodal temperature corresponds to phase separation through local scale fluctuations. It is best detected by the SANS method. The binodal temperature corresponds to phase separation at a large length scale. It is best detected by light scattering. The binodal temperature can also be detected by SANS.
2. Scattering and polymer mixture thermodynamics are related by the following equation: $(1/k_B T) (\partial^2 G / \partial \phi_1^2) = S^{-1}(Q=0)$. Here G is Gibbs free energy density, ϕ_1 is the volume fraction of component 1 and $S(Q=0)$ is the scattering factor for $Q=0$ (i.e., in the thermodynamics limit).
3. The spinodal condition is defined by the inflection point of $G(\phi_1)$ vs ϕ_1 where G is the Gibbs free energy density. This condition is expressed as $\partial^2 G / \partial \phi_1^2 = 0$.
4. The thermodynamics of phase separation of a polymer solution can be described by the Flory Huggins theory with $n_2 = 1$ (assuming that component 2 is the solvent). This tends to skew the phase diagram for polymer solutions towards the dilute limit. The critical point for polymer solutions takes place at low polymer volume fractions.
5. The spinodal region is underneath the spinodal line in the phase diagram (temperature T vs volume fraction ϕ_1). The nucleation and growth region is between the binodal and spinodal lines.
6. The RPA breaks down when the sample is in the two-phase region.
7. A fully phase separated polymer blend is characterized by a droplet morphology (droplets of one component in the medium of the other). A fully phase separated sample is also “hazy” since the droplets’ size becomes comparable to the wavelength of visible light (fraction of a micron).